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TRANSACTIONS

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Nº. I.

*Experiments and Observations relating to the Analysis of
Atmospherical air, by the Rev. Dr. J. PRIESTLEY.*

Read Feb. 5, 1796. **I**T is an essential part of the antiphlogistic theory, that in all the cases of what I have called the *phlogistication of air* there is simply an absorption of the dephlogisticated air, or, as the advocates of that theory term it, the *oxygen* contained in it, leaving the phlogisticated part, which they call *azote*, as it originally existed in the atmosphere. Also, according to the principles of this system, *azote* is a simple substance, at least not hitherto analysed into any other: They therefore suppose that there is a determinate proportion between the quantities of oxygen and azote in every portion of atmospherical air, and that all that has hitherto been done has been to separate them from one another. This proportion they state to be twenty seven parts of oxygen and 73 of azote, in 100 of atmospherical air.

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But in every case of the diminution of atmospherical air in which this is the result, there appears to me to be something emitted from the substance, which the anti-phlogistians suppose to act by simple absorption, and therefore that it is more probable that there is some substance, and the same that has been called phlogiston, or the *principle of inflammability* (being common to all bodies capable of combustion, and transferable from any one of them to any other) emitted, and that this phlogiston uniting with part of the dephlogisticated air forms with it part of the phlogisticated air which is found after the process; and in some cases there is more of this, and in others less. Also, in some cases fixed air is the result of the union of the same constituent principles.

A mixture of iron filings and sulphur, which, with a little water, has been commonly made use of to diminish and phlogistificate air, and probably many other substances which produce the same effect, if they be continued in the air after the diminution has advanced to its *maximum*, occasion an increase of the quantity, by an addition of inflammable air. This mixture I find to have the same effect when it is long confined in nitrous air, or in fixed air; and therefore it is probable that the same would be the case if it were confined in any other kind of air, or in vacuo. It therefore, seems natural to infer that the same principle which constitutes inflammable air was from the first exhaling from the mixture, but that it did not actually form inflammable air till there was no more dephlogisticated air for it to unite with, and thereby form phlogisticated air. The experiments from which this conclusion is drawn are recited in my former publications, and I have lately repeated them with particular attention, and the same result. I have also lately observed that by heating bones made black by burning without access of air, in atmospherical air, there is, after the period

period of greatest diminution, an increase of the quantity, and that it is then found to contain a mixture of inflammable air.

That something is really emitted from the iron filings and sulphur, when it is in a state of diminishing air is evident from the strong and offensive *smell* which at that time this mixture has. Flowers also, and especially those which have the strongest smell, I have observed to phlogificate air. Moreover, the iron filings and sulphur when nearly dry, emit a visible dense vapour, which appears by its smell to be vitriolic acid air, which I have observed to have the power of diminishing and phlogificating air; owing no doubt, in part to its imbibing the dephlogificated part of it, and with it forming common vitriolic acid; but at the same time part of its phlogiston may unite with another part of the dephlogificated air, and with it form phlogificated air.

Iron filings and sulphur, as well as phosphorus, and most of the other substances which have been generally used for the purpose of phlogificating atmospheric air, do likewise imbibe the dephlogificated air contained in it, and thereby gain an addition of as much weight as the air has lost. But this is not the case with *black bones* heated in air, which by this means become white; and as nothing in them is volatile, except that which constitutes their blackness, I thought they would be a very convenient substance with which to make these experiments.

These bones gained no addition of weight in the process, and when they are used, the diminution of the air is by no means so great as in the other cases, though the air that is left is completely phlogificated. This is probably in consequence of the fixed air (formed by the union of the dephlogificated air with the phlogiston emitted from the bones) not being readily imbibed by

the water, or any other substance with which it is then in contact; so that a better opportunity is given to the phlogiston emitted from the bones to unite with that air in a different manner, and form phlogisticated air, which is therefore after the process found in a greater proportion than in the other cases, to which alone a due attention has hitherto been given. When these bones are heated over lime water, there is a copious precipitation of the lime. Here I would observe that the phlogiston necessary to form this fixed air could only come from the bones in becoming white, as they had been calcined in as great a degree of heat as I could produce, so that no kind of air could have been expelled from them while excluded from access of air.

Having by means of a burning lens heated 140.5 grains of well burned black bones in 23.75 ounce measures of air, it was reduced to 20 ounce measures, completely phlogisticated, without any mixture of fixed or inflammable air in it. According to this experiment, the quantity of pure air in 100 ounce measures of atmospherical air was only 15.78 parts instead of 27.

Heating 267 grains of these bones in 30 ounce measures of air, it was reduced to 25.5 ounce measures completely phlogisticated, which was in the proportion of 15 parts of dephlogisticated air in 100 of atmospherical. In these experiments with bones there is sometimes a small loss of weight, owing, I doubt not, to something besides phlogiston being expelled from them by the intense heat of the lens; and during the process I could perceive a slight vapour rising from them. When I managed the heat so that it was not more than necessary to whiten the bones, they neither gained nor lost any weight; at least the loss was very inconsiderable.

I had similar results from experiments made with small polished *steel needles*. For when they were heated so as
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only to become blue, and were not melted, they gained very little, if any, weight, and diminished the air only in about the same proportion with the black bones.

Having by means of a burning lens heated 200 grains of the polished needles in 24 ounce measures of air (in consequence of which they became of a dark colour) they neither gained nor lost any weight, and the air was reduced to 19.5 ounce measures, almost completely phlogisticated. I heated the same quantity of these needles in 16.75 ounce measures of air, when it was reduced to 13.5 ounce measures, completely phlogisticated without any mixture of fixed or inflammable air in it; so that the diminution was in the proportion of 19.4 parts in one hundred. In another experiment 24.75 ounce measures of air were reduced to 20.25 ounce measures nearly phlogisticated. It is evident, therefore, from these experiments, that more phlogisticated air is found after this process, than after that with the iron filings and sulphur.

Because by heating the needles over a quantity of water they might attract moisture, which cannot be expelled from them without some difficulty, I heated 200 grains of the same needles in the open air, till they had assumed exactly the same appearance with those that had diminished the air in the preceding experiments, and found that they had neither gained nor lost any sensible weight. The same was the result of whitening a quantity of black bones in the open air. But to make this experiment with accuracy, the bones should be calcined with the greatest degree of heat, and made white with the least.

In one experiment with very thin pieces of malleable iron (viz. iron turnings) 38.5 ounce measures of air were reduced to 31.5 measures, wholly phlogisticated, which is in the proportion of the loss of 19.5 parts in 100. I could not perceive that the iron had gained or
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lost any weight ; whereas, if it had imbibed the air that had disappeared, or the water, of which, as I have shewn, the air principally consists (as it would have done if it had been melted in the process) it ought to have gained 4.2 grains.

There was not, however, the same certainty in the experiments with the needles, and still less with the iron, as in those with the bones. They generally gained a little weight, and diminished the air more than the bones. The reason of this uncertainty might be that they were sometimes heated too much ; and sometimes fine scales were thrown from them, which were indeed sometimes visible when, in floating about within the vessel, they crossed the sun beams, and both in the experiments with the needles and those with the bones a vapour visibly rose from them. When the needles were heated over lime water, a thick crust was formed upon it ; but there was not such a precipitation of the lime as in the experiments with the bones.

That the phlogistication of nitrous acid is owing, in some cases, to its *imbibing* something, and not always to its *parting* with any thing, which the antiphlogistians maintain is evident from its becoming phlogisticated by imbibing nitrous air. This I have observed that it does with the greatest rapidity, leaving in some cases not more than one 18th part of the original quantity. M. Fourcroy supposes (*Philosophie Chymique*, p. 76) that the conversion of the common nitrous acid into the phlogisticated is always occasioned by its parting with oxygen. That this is sometimes the case I have demonstrated in my experiments with heating it in long glass tubes ; but in the present case it is not possible that the acid should have parted with any thing, and least of all with *oxygen*, since the small residuum of nitrous air is pure *azote*. I shall here observe, what I did not before, that the absorption
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of nitrous air by nitrous acid is attended with a considerable degree of heat.

That phlogisticated air, or azote, is not a simple substance, but consists of phlogiston (or whatever is the proper element of inflammable air) and of dephlogisticated air, is probable from several experiments that seem to have been overlooked by the antiphlogistians, such as the following. A mixture of dephlogisticated and inflammable air being kept a long time was found by M. Metherie to contain a considerable portion of phlogisticated air, as appeared by the difference of the residuums after exploding a part of the mixture when first made, and another part some time afterwards. I had also found that a mixture of dephlogisticated and inflammable air suffers a considerable diminution in a course of time, though they will not wholly incorporate. But I have lately found that these two kinds of air unite completely by being confined some time together in a moist bladder.

Having mixed equal quantities of those kinds of air, I put them into a bladder, which I left floating in a trough of water, and found, after about a fortnight, that the quantity was considerably diminished; and examining it, I found it to be almost wholly phlogisticated, though there was something slightly inflammable in it. On this I put equal measures (but omitted to note the quantity) of each of the kinds of air into another bladder, and after about three weeks, found it reduced to 12.5 ounce measures, all pure phlogisticated air, without any mixture of fixed or inflammable air that I could perceive.

I have likewise hit upon another method of forming phlogisticated air by the union of dephlogisticated and inflammable air, viz. by exposing the latter to a surface of rusted iron, which is known to become so by imbibing pure air. Twenty ounce measures of inflammable air were

were confined in a phial containing pieces of rusted iron from the 18th of August to the 6th of October, when it was reduced to 9 ounce measures, and was but slightly inflammable. The iron, from being red, was then become of a very dark colour. Another quantity of inflammable air treated in the same manner from, I believe, the 6th of October, was in the 2d of December found to be completely phlogificated. In these experiments the iron and the air were confined by water. Afterwards, putting 7 ounce measures of inflammable air to pieces of rusted iron confined by mercury, it was, in about a week, almost wholly absorbed. I then filled up the vessel again with inflammable air, and when the diminution proceeded no farther, I examined it, and found 5 ounce measures of air completely phlogificated.

Charcoal, as well as phlogificated air, I have no doubt, contains the element of dephlogificated air, as well as phlogiston, since by its union with steam it takes the form of fixed air, as well as that of inflammable air, and one element in the composition of fixed air is dephlogificated air. And when I made hot charcoal imbibe inflammable air by introducing pieces of it into jars of this air confined by mercury, and afterwards expelled it by plunging the charcoal in water, that which came out of it was phlogificated air. Yet I think I recollect that the result of this experiment has sometimes been inflammable air, the same that the charcoal had imbibed.

I know of no case of the simple absorption of air, but which, like that by water, respects all kinds of air, though with a preference of that which is dephlogificated; but not so as to take this kind *only*, and leave all the phlogificated air that was mixed with it. Otherwise it would have been in our power to ascertain with exactness the real proportion of both the kinds of air in the atmosphere

phere. For want of this the nearest approximation that we can make appears to me to be by the use of nitrous air.

Since when two measures of pure nitrous air are mixed with one measure of pure dephlogisticated air, they both, as nearly as possible, disappear, and form nitrous acid, which is imbibed by the water in which the mixture is made, it is evident that little or no phlogisticated air is necessarily formed in this process; and when it is conducted properly, there will appear to be a much greater proportion of dephlogisticated air in the atmosphere than has been supposed, and enough to be converted into phlogisticated air in the process above mentioned. But a considerable *time* is necessary for this purpose; because the diminution continues much longer than has been hitherto imagined.

The difference between the degree of diminution of atmospheric air by a mixture of nitrous air, with, or without, *agitation*, is very considerable. In general, without agitation, equal measures of each will occupy the space of 1.25 measures, but with agitation only 1.01; and if the computation be made from this last *datum*, it will give the proportion of dephlogisticated air to be 27 parts in 100, and consequently that of the phlogisticated air 73. But by keeping the mixture a longer time, the diminution will proceed to about 0.6 of a measure which will give 46.6 for the proportion of dephlogisticated air, and 53.4 for that of the phlogisticated air in the atmosphere.

This diminution in the mixture of nitrous and atmospheric air, which is effected in the course of time, is various, depending, no doubt, on several circumstances which I have not yet been able to ascertain. What I have actually observed is as follows,

On the 21st of July I mixed equal quantities of nitrous and atmospheric air; when, with agitation, they oc-
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cupied the space of 1.01. Examining the mixture at different times, I observed that the diminution kept advancing till some time before 24th of August, when it occupied the space of only 0.545. Another mixture made in the same manner was 0.54, and another 0.65. At the same time I found other mixtures made without agitation, which at first occupied the space of 1.25, were in one case 0.75, another 0.72 and another 0.65.

The reason why I apprehend the diminution goes on so long is, that time is requisite for the action of the phlogiston in the nitrous air upon the dephlogisticated part of the atmospheric air, in order to the conversion of the whole of it into nitrous acid, in consequence of this part being intimately diffused through the phlogisticated part, by which it is, as it were, protected from its action, which is similar to many other chemical processes. It is for the same reason that the diminution is much greater with agitation than without it, as the parts disposed to unite are thereby brought into better contact.

When atmospheric air is exploded together with inflammable air, the diminution never proceeds so far as when nitrous air is mixed with it; because in this case phlogisticated air, as well as nitrous acid, is formed by their union; and, as I have shewn, the greater is the proportion of the inflammable air employed, the greater will be the proportion of phlogisticated air in the residuum. This mixture, however, will go on diminishing for some time, though not so far as that with the nitrous air; because part of this produce being nitrous acid, as I have shewn in a former course of experiments, it will require time to be formed, as well as when the nitrous air is employed.

Having made a mixture of equal parts of inflammable and atmospheric air, and exploded them on the 3d of August, I observed that it then occupied the space of

1.35 measures, and on the 2d of September, when I perceived that the diminution would proceed no farther, it was 1.14 which, though considerable, was far short of the diminution produced by an equal bulk of nitrous air.

Though, in the experiments recited above with the *calcined bones*, and the *steel*, neither of these substances appeared to have lost any weight that I was able to ascertain, it does not follow that nothing was emitted from them. For *light* and *heat* are almost universally allowed to be *substances*, though no person has been able to weigh them. Besides the quantity of the materials that I made use of might be too small for the purpose. What is most important in the experiments is that, since the diminution of the air was effected by heating those substances, and they did not *gain* any weight in the process, the phlogification of air is not the absorption of any part of it by the substance which produces that effect, as the antiphlogistic theory supposes.

Nº. II.

Farther Experiments relating to the Generation of Air from Water, by Rev. Dr. J. PRIESTLEY.

Read Feb. 19, 1796. **I**N a late publication, containing an account of some experiments relating to *the generation of air from water*, I mentioned three different processes in which air was produced from the same water, without any perceivable limit.

The first process was converting the whole of a quantity of water into steam, in the common method of boiling;